Deuterium fractionation on interstellar grains studied with the direct master equation approach

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ABSTRACT
We have studied deuterium fractionation on interstellar grains with the use of an exact method known as the direct master equation approach. We consider conditions pertinent to dense clouds at late times when the hydrogen is mostly in molecular form and a large portion of the gas-phase carbon has already been converted to carbon monoxide. Hydrogen, oxygen, and deuterium atoms, as well as CO molecules, are allowed to accrete onto dust particles and react there to produce various stable molecules. The surface abundances, as well as the abundance ratios between deuterated and normal isotopomers, are compared with those calculated with the Monte Carlo approach. We find that the agreement between the Monte Carlo and the direct master equation methods can be made as close as desired. Compared with previous examples of the use of the direct master equation approach, our present method is much more efficient. It should now be possible to run large-scale gas-grain models in which the diffusive dust chemistry is handled "exactly".

Key words: molecular processes – ISM: clouds – ISM: molecules.

1 INTRODUCTION

Rate equations have long been used in modelling the surface chemistry that occurs on cold dust particles in the interstellar medium (Pickles & Williams 1977; Hasegawa, Herbst & Leung 1992). It has been pointed out (Charnley, Tielens & Rodgers 1997) that, in the case when the average number of reactive species on a grain is sufficiently small, the rate equations may not be suitable to describe the system, since they do not take into consideration its discrete nature. One alternative is to use a Monte Carlo approach (Tielens & Hagen 1982; Charnley et al. 1997; Caselli et al. 2002; Charnley 2001).

Recently another approach to this problem (Green et al. 2001; Biham et al. 2001), has been proposed. Like the Monte Carlo method, this approach is based on a master equation. But, unlike the Monte Carlo technique, the master equation is directly converted into differential equations. In particular, the rate equations for the population of highly reactive species with small surface abundances are replaced by sets of differential equations for the probability that certain number of these atoms or molecules exist on the surface at the same time. One advantage of this new exact approach is its easy coupling

with the differential rate equations used to model the gas-phase chemistry. A comparison of the two approaches is to be found in Stantcheva, Shematovich & Herbst (2002).

We have, so far, successfully applied the direct master equation approach to a system consisting of H and O atoms and CO molecules accreting onto a grain surface, and reacting to form a variety of reaction products (Stantcheva et al. 2002). In this paper, we report an expansion of the system to include D atoms accreting onto the surface and reacting with the other reactive surface species to produce deuterated isotopomers. The system is identical to that studied in Caselli et al. (2002) with modified rate equations and a Monte Carlo approach. A somewhat smaller network of reactions was utilised by Charnley et al. (1997). As opposed to Caselli et al. (2002), we concentrate on the doubly, triply and quadruply-deuterated species which we believe are likely candidates for observation in highly fractionated low-mass protostellar sources (Parise et al. 2002). The main purpose of this paper; however, is to show how the direct master equation method can be used efficiently.

The paper is organised as follows. First, in Section 2 a short description of the system under investigation is given. The theory, including the formulae used in the calculations, is given in Section 3. Section 4 presents the results, and is followed by a discussion in Section 5.

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Table 1. H, O, and CO gas-phase abundances (cm^{-3}) utilised

Abundance n	Low	Intermediate	High
H	1.15	1.15	1.10
O	0.09	0.75	7.0
CO	0.075	0.75	7.5
D	0.3	0.3	0.3

Table 2. Assorted rates for selected species at 10 K

Species	k_{acc} ($cm^3 s^{-1}$)	t_{evap}^{-1} (s^{-1})	t_{diff}^{-1} (s^{-1})
H	1.45(-5)	1.88(-3)	5.14(+4)
D	1.02(-5)	1.67(-4)	3.92(+2)
O	3.62(-6)	2.03(-23)	4.24(-5)
CO	2.73(-6)		

2 THE CHEMICAL NETWORK AND PHYSICAL CONDITIONS

We have considered a system in which H, O, and D atoms and CO molecules accrete onto the grain surface and react to form the stable molecules H_2, HD, D_2, H_2O, HDO, D_2O, H_2CO, HDCO, D_2CO, CH_3OH, CH_3OD, CH_2DOH, CH_2DOD, CHD_2OH, CHD_2OD, CD_3OH, CD_3OD, O_2, CO_2, and the highly reactive radicals OH, OD, HCO, DCO, H_3CO, H_2DCO, HD_2CO, and D_3CO. The system pertains to old dense interstellar clouds, in which hydrogen is mostly molecular and carbon is mostly in the form of CO. The calculations were performed mainly at a temperature T=10 K, for a period of 10^4 years, and fixed gas-phase abundances of the accreting species, an approximation justified by the relatively short period of evolution of the surface chemistry compared with the time scale of the gas-phase chemical processes. At times even earlier than 10^4 yr, a steady-state condition is reached in which the surface populations of the stable species grow linearly with increasing time while the reactive species have fixed populations. The number of available sites per grain, which helps to define the diffusion rates, was taken to be 10^6; this number refers to so-called classical grains with a size of 0.1 μm.

Three different sets of values for the gas-phase densities of H, O, CO, were used throughout the calculations. Given in Table 1, these sets of values are referred to as the low, intermediate, and high density cases because they were derived from gas-phase models at total densities of 10^3, 10^4, and 10^5 cm^{-3}, respectively. In all cases, the concentration of H is near 1 cm^{-3}. Unless stated to the contrary, all results are for a gas-phase abundance for D of 0.3 cm^{-3}. This very high value relative to the atomic H abundance is presumably produced via fractionation in the cold gas, although current gas-phase models cannot easily reproduce such a value (Roberts, Herbst & Millar 2002). Variations in the atomic deuterium abundance are also considered.

In calculating the accretion, desorption, and diffusion rates of the surface species, we followed the methods used in Hasegawa et al. (1992) – see also Caselli et al. (2002); Caselli, Hasegawa & Herbst (1998) – and used their values for the parameters necessary for the calculations. All particles were considered to diffuse over the surface solely via thermal hopping except for H and D atoms, for which quantum tunnelling was also considered. The rates used for diffusion are the so-called fast rates (Stantcheva et al. 2002) because these magnify the differences between exact and approximate methods for studying diffusive surface chemistry. Table 2 shows the accretion, evaporation, and diffusion rates over an entire grain for the accreting species in the model. Note that at the temperatures considered, the other heavy species in the model do not diffuse or evaporate at non-negligible rates.

Table 3. Surface reactions in the H,O,CO model.

Number	Reaction			E_a (K) [a]
1	H + H	$\longrightarrow$	H_2	
2	H + O	$\longrightarrow$	OH	
3	H + OH	$\longrightarrow$	H_2O	
4	H + CO	$\longrightarrow$	HCO	2000
5	H + HCO	$\longrightarrow$	H_2CO	
6	H + H_2CO	$\longrightarrow$	H_3CO	2000
7	H + H_3CO	$\longrightarrow$	CH_3OH	
8	H + D	$\longrightarrow$	HD	
9	H + OD	$\longrightarrow$	HDO	
10	H + DCO	$\longrightarrow$	HDCO	
11	H + HDCO	$\longrightarrow$	H_2DCO	1965
12	H + D_2CO	$\longrightarrow$	HD_2CO	1925
13	H + H_2DCO	$\longrightarrow$	CH_2DOH	
14	H + HD_2CO	$\longrightarrow$	CHD_2OH	
15	H + D_3CO	$\longrightarrow$	CD_3OH	
16	O + O	$\longrightarrow$	O_2	
17	O + CO	$\longrightarrow$	CO_2	1000
18	O + HCO	$\longrightarrow$	CO_2 + H	
19	O + D	$\longrightarrow$	OD	
20	O + DCO	$\longrightarrow$	CO_2 + D	
21	OH + D	$\longrightarrow$	HDO	
22	CO + D	$\longrightarrow$	DCO	1930
23	HCO + D	$\longrightarrow$	HDCO	
24	H_2CO + D	$\longrightarrow$	H_2DCO	1799
25	H_3CO + D	$\longrightarrow$	CH_3OD	
26	D + D	$\longrightarrow$	D_2	
27	D + OD	$\longrightarrow$	D_2O	
28	D + DCO	$\longrightarrow$	D_2CO	
29	D + HDCO	$\longrightarrow$	HD_2CO	1758
30	D + D_2CO	$\longrightarrow$	D_3CO	1713
31	D + H_2DCO	$\longrightarrow$	CH_2DOD	
32	D + HD_2CO	$\longrightarrow$	CHD_2OD	
33	D + D_3CO	$\longrightarrow$	CD_3OD	

[a] See Caselli et al. (2002)

The surface reactions used in our model as well as any non-zero activation energies E_a are given in Table 3. More details can be found in Caselli et al. (2002).

3 MASTER EQUATION FOR THE SYSTEM

In the direct master equation method, the system corresponding to the grain surface is represented by a multitude of states that represent different possible populations of the surface species. In one state we might have 0 particles of the species A, 1 particle of the species B, 2 particles of the species C, ..., whereas a different state might consist of 1

particle of A, 0 of B, 2 of C, ... With each state, we associate a probability for the system to be in this state, and we develop equations for the rate at which these probabilities change (the master equation). Basic to the approach is the fact that the populations of some of the surface species are correlated. As a consequence, the method, at least formally, requires the consideration of the evolution of the system as a whole, as opposed to the rate equation approach, in which the evolution of the average population of any given species is followed separately.

In the most general case, all the surface species are taken into consideration in each state of the system. Since the standard rate equations, however, give a sufficiently accurate description of the evolution of high-abundance species (Stantcheva et al. 2002), the inclusion of these species in the master equation will impose an unnecessarily heavy load on the computing resources given the need to integrate many coupled equations simultaneously. Thus, a more practical approach involving fewer coupled equations is to include only the highly reactive and low-abundance surface species in the master equation, and to use rate-like equations to solve for the surface populations of the rest of the species. As a guide to determine which species should be included in the master equation, one can use the results obtained via rate equations and, if available, Monte Carlo simulations. More generally, these species are reactive atoms and radicals, especially those that are precursors of major grain species. Here we include the 11 species H, O, D, OH, OD, HCO, DCO, CH_3O, CH_2DO, CHD_2O, and CD_3O. We enumerate these from 1 to 11 and refer to them as "probabilistic". The remainder of the species are referred to as normal and are treated via rate-like equations.

Once we have determined the probabilistic species, we assign a probability $P(i_1, \ldots, i_{11})$ to any state $\{i_1, \ldots, i_{11}\}$ that consists of i_1 H atoms, i_2 O atoms, i_3 D atoms, i_4 OH molecules, $\ldots$, i_{11} CD_3O molecules, and solve the master equation, which consists of equations for the rate of change of the state probabilities $P(i_1, \ldots, i_{11})$. These equations are of the form

$$\frac{dP}{dt}(i_1, \ldots, i_{11}) =$$

$$\sum_{\{X\}} k_{\mathrm{acc}}(X) n(X) \left[P(..., i_j - 1, ...) - P(..., i_j, ...) \right]$$

$$+ \sum_{\{X\}} t_{\mathrm{evap}}^{-1}(X) \left[(i_j + 1) P(..., i_j + 1, ...) - i_j P(..., i_j, ...) \right]$$

$$+ \sum_{\{X,Y\}} k_{X,Y} (i_j + 1)(i_k + 1) P(..., i_j + 1, ..., i_k + 1, ...)$$

$$- \sum_{\{X,Y\}} k_{X,Y} (i_j)(i_k) P(..., i_j, ..., i_k, ...)$$

$$+ \sum_{\{X\}} k_{X,X} \frac{(i_j + 2)(i_j + 1)}{2} P(..., i_j + 2, ...)$$

$$- \sum_{\{X\}} k_{X,X} \frac{i_j(i_j - 1)}{2} P(..., i_j, ...) .$$

(1)

In eqs. (1), i_j corresponds to the surface abundance

of the species X, i_k to that of the species Y, $n(X)$ is the gas-phase abundance of X, and $k_{\mathrm{acc}}(X)$, $t_{\mathrm{evap}}^{-1}(X)$, and $k_{X,Y}$ are the accretion and evaporation rates of X, and the rate coefficient for reaction between X and Y, respectively (Hasegawa et al. 1992). In the units used here (Caselli et al. 1998), the rate coefficient is simply the sum of the the diffusion rates of X and Y over the entire grain. The first two terms on the right-hand side of eq. (1) represent the changes in the probability with time due to accretion and evaporation processes. The subsequent terms account for the changes due to reactions between two probabilistic species, both non-identical and identical. It is important to note that there should be two more terms on the right-hand side of eq. (1), which are present in our calculations but are not given here for considerations of simplicity. The first of these terms takes into account the change of the probability due to reactions between a probabilistic and a normal species, such as H+CO⟶HCO. The second accounts for (slow) reactions between two normal species, which have at least one probabilistic species as a product. In our current model there are no reactions of the latter type. In addition to these simplifications, we have also not indicated changes to more than two stochastic species in any term although there are reactions in which the populations of three such species can change (e.g. O + HCO).

The solution of eqs. (1) gives the probabilities for all the states, which, in turn, allows the calculation of the average abundance, or number of species per grain, of each probabilistic species, $\langle N_X \rangle$, as well as any necessary correlation terms, of the form $\langle N_X N_Y \rangle$. These entities, then, are substituted into the equations used to solve for the abundances of the normal species. Although the latter equations are very similar to the widely used rate equations, they bear important differences. Equations (2) and (3) are the expressions for the average abundances of H_2 and H_2CO (both being normal species):

$$\frac{d\langle N_{H_2} \rangle}{dt} = - t_{\mathrm{evap}}^{-1}(H_2) \times \langle N_{H_2} \rangle$$
$$+ 0.5\, k_{H,H} \times \langle N_H(N_H - 1) \rangle, \quad (2)$$

$$\frac{d\langle N_{H_2CO} \rangle}{dt} = + k_{H,HCO} \times \langle N_H N_{HCO} \rangle$$
$$- k_{H,H_2CO} \times \langle N_H \rangle \times \langle N_{H_2CO} \rangle. \quad (3)$$

It can be seen that, unlike regular rate equations, both correlated abundances and terms in which 1 is subtracted from an abundance appear. The rate-like equations are obtained by summation over single and correlated probabilities for the relevant stochastic species involved in the formation and depletion of major species (Biham et al. 2001; Green et al. 2001; Stantcheva et al. 2002).

To propagate the system forward in time, both the master equation and the rate-like equations must be solved simultaneously. Since the probabilistic species have very low abundance, the probability for the system to be in states that contain high abundances of these species must be very small. It is reasonable, then, to neglect such states and limit our consideration to those that comprise only very few particles. For this purpose, we choose a set of parameters, $\{N_1, N_2, \ldots, N_{11}\}$ and N_{tot}, such that we neglect every state, $\{i_1, i_2, \ldots, i_{11}\}$, for which the following conditions hold true:

$$i_j \quad > \quad N_j \quad \text{, for any } j, \text{ or} \tag{4}$$

$$\sum_j i_j \quad > \quad N_{\text{tot}} . \tag{5}$$

Because the first three particles in $\{i_1, i_2, \ldots, i_{11}\}$ correspond to H, O, and D, we require that $N_1, N_2,$ and N_3 be equal to at least 2 so that molecular hydrogen, oxygen and deuterium can be produced. Thus, the set of minimum values for the upper limits N_j is $\{2,2,2,1,1,\ldots,1\}$. If we choose $\{N_j\}$ to be equal to this set of minimum values, condition (4) will eliminate all but $\mathcal{N} = 3^3 \times 2^8 = 6912$ possible states of the system. This is still a very large number of coupled differential equations! A strong reduction in this number, however, can be obtained by applying condition (5), *which we have not done previously.* Of course, the number of states will be dependent on the value of N_{tot} chosen. Clearly, any meaningful value of N_{tot} must be larger than or equal to each N_j and smaller than their sum, $\sum_j N_j$. If N_{tot} is taken to be 2, the number of states will be 70 for the set of limits $\{2,2,2,1,1,\ldots,1\}$.

To understand how this number is determined, consider the following argument. Let the number of probabilistic particles be m. For the chosen N_j and N_{tot}, there will be four different groups of states: the first group, $[0,0,\ldots,0]$, consisting of only one state $\{0,0,\ldots,0\}$, the second group, $[1,0,\ldots,0]$, consisting of m different states, the third group, $[1,1,0,0,\ldots,0]$, consisting of $\frac{m(m-1)}{2!}$ states, and the fourth group, $[2,0,\ldots,0]$, consisting of only 3 states – $\{2,0,\ldots,0\}$, $\{0,2,0,\ldots,0\}$, and $\{0,0,2,0,\ldots,0\}$. In our model $m{=}11$, so that the total number of states is $1 + 11 + 55 + 3 = 70$.

Although analytical formulae can be derived for the number of states determined by other specific values for m, $\{N_1, N_2, \ldots, N_m\}$ and N_{tot}, we choose to determine this number by a computer subroutine.

4   RESULTS

Table 4 shows a comparison between the surface populations (in monolayers per grain) of normal (stable, non-deuterated) species calculated via the direct master equation (ME) and the Monte Carlo (MC) approaches for the low, intermediate, and high density cases. To use the former method, all N_j were set to their minimum values except for N_2 and N_4, which correspond to O and OH. The calculations showed the latter two average abundances to be close to unity in some cases so that higher values for their upper limits had to be considered.

Table 4 also shows the values of N_2 and N_4 for the three cases as well as the limit N_{tot} for the total number of probabilistic species and the total number of states $\mathcal{N}$. One can see that for the high and intermediate density cases, the direct master equation method requires the solution of more than 816 coupled differential equations since the number $\mathcal{N} = 816$ does not include the rate-like differential equations for the stable species.

For the low and intermediate density cases, the agreement between the master equation and the Monte Carlo approaches is excellent, and the master equation approach outperforms the Monte Carlo calculation in terms of computer time, dramatically so for the low density limit. For

the high density case, the agreement is not as excellent, but the results of the two methods deviate by at most 10%. This small deviation can be explained by the high abundance of O and OH on the surface, a condition that requires that higher values for N_2 and N_4, and consequently many more states, be considered in the master equation approach. In general, the agreement between the two formally exact approaches can be made as good as desired by considering sufficiently high values for the N_j and for N_{tot}. This, however, will mean longer times for the master equation calculations to run, so one needs to find the right balance between the desired accuracy and the usage of computing resources. In general, it is a current weakness of the master equation approach that there is no obvious algorithm to determine the proper upper limit to the number of states to be considered.

The fractionation ratios, fXD, are defined as the ratio between the abundances of the deuterated and the normal isotopomers. The results for the fractionation ratios are given in Table 5 for the three cases discussed previously. The agreement between the two methods is reasonable but not perfect; here the major problem lies in the Monte Carlo approach, which is not accurate for small populations. Indeed, for some of the smaller fractionation ratios, no values could be calculated with this method since populations less than unity are not allowed. As an example, consider the case of CHD_2OH at intermediate density. From the tables, one sees that the overall population of this molecule in the Monte Carlo approach is approximately 140 molecules. While the random (square-root) error is thus at the 10% level, the actual error is considerably greater and is probably large enough to cover the 30-40% difference between the two methods of calculation.

We have also used the direct master equation approach to model the chemistry in the temperature range 10-20 K for the high density case. Fig. 1 shows the fractionation ratio f of doubly and multiply deuterated isotopomers in this temperature range, while a plot of the mole fraction of the normal isotopomers vs. temperature is given in Fig. 2. The parameters for the calculation (number of states, etc.) are the same as shown in Table 4. It can be seen that as the surface temperature increases from 10 to 20 K, the species (H_2CO, CH_3OH) made by hydrogenation involving reactions with activation energy decline sharply in abundance. This non-intuitive result derives from the fact that at higher temperatures, H atoms evaporate before they react. In addition, for most species, the fractionation ratios decline sharply with increasing temperature, especially for isotopomers that must be formed by reactions with activation energy and involving D atoms, since these atoms tunnel more poorly than their H counterparts and are more likely to evaporate.

Finally, the dependence of the fractionation ratios for doubly and multiply deuterated isotopomers on the ratio of atomic deuterium to hydrogen is shown in Fig. 3 for a 10 K cloud at high density. The abscissa is actually the ratio of the accretion rate of atomic D to that of atomic H; this is equal to the ratio of the gas-phase abundances multiplied by a factor of $2^{-0.5}$ that derives from the relative speeds of D and H. Not surprisingly, the fractionation ratios increase as the D/H accretion ratio increases, with the slope proportional to the number of deuterium atoms in the isotopomer. In fact, the results in Fig. 3 lie very close to the
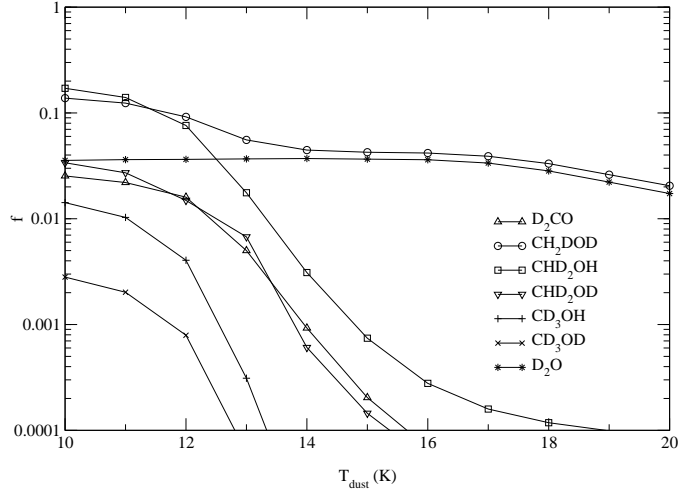
Figure 1. Fractionation ratios f vs. $T_{dust}(K)$ at 10^4 yr for the high density case, with n(D)=0.3 cm^{-3}, computed with the direct master equation technique. The results lie close to a simple analytical limit near 10 K.
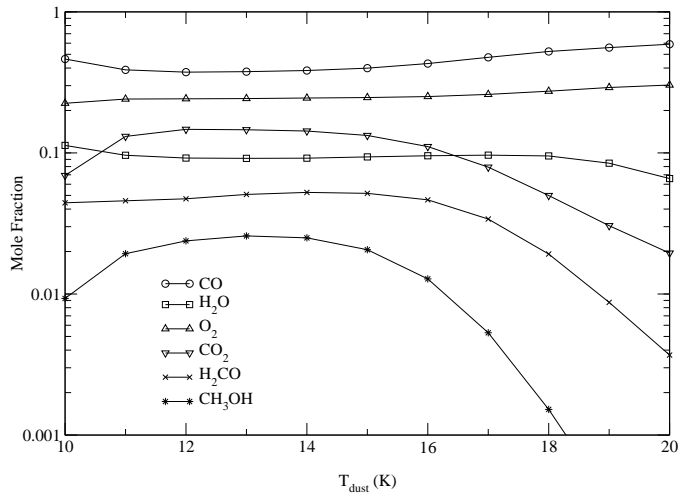
Figure 2. Mole fractions of major surface species vs. $T_{dust}(K)$ at 10^4 yr for the high density case, computed with the direct master equation technique.

Table 4. Populations in mono-layers at 10^4 yr and 10 K.

Species	High Density		Interm. Density		Low Density	
	MC	ME	MC	ME	MC	ME
CO	5.0	4.9	0.00	0.00	0.0	0.0
H_2O	1.4	1.2	0.45	0.45	0.070	0.069
O_2	2.7	2.4	0.080	0.079	0.0013	0.0013
CO_2	0.67	0.71	0.055	0.055	7.7(-4)	7.2(-4)
H_2CO	0.44	0.44	0.0	0.0	0.0	0.0
CH_3OH	0.088	0.095	0.42	0.42	0.046	0.046
Total abundance	11.1	10.5	1.37	1.36	0.165	0.164
$N_2=N_O$		4		4		2
$N_4=N_{OH}$		4		4		1
N_{tot}		4		4		3
$\mathcal{N}$		816		816		265
CPU sec (Cray SV1)	789	313	366	245	366	14

Table 5. Abundance ratios f at 10^4 yr and 10 K.

Species	High Density		Interm. Density		Low Density	
	MC	ME	MC	ME	MC	ME
fHDCO	0.33	0.34	...	...	...	...
fD$_2$CO	0.026	0.027	...	...	...	...
fCH$_3$OD	0.20	0.20	0.19	0.18	0.18	0.18
fCH$_2$DOH	0.70	0.71	0.19	0.19	0.19	0.19
fCH$_2$DOD	0.14	0.14	0.034	0.034	0.034	0.034
fCHD$_2$OH	0.17	0.18	3.3(-4)	2.1(-4)	2.6(-4)	1.4(-4)
fCHD$_2$OD	0.034	0.035	6.4(-5)	3.9(-5)	...	2.5(-5)
fCHD$_3$OH	0.014	0.015	...	5.6(-8)	...	2.3(-8)
fCHD$_3$OD	0.0025	0.0029	...	1.0(-8)	...	4.3(-9)
fHDO	0.39	0.38	0.38	0.38	0.39	0.39
fD$_2$O	0.038	0.036	0.036	0.036	0.036	0.038

very simple limit (Tielens 1983; Brown & Millar 1989) in which all H and D atoms that accrete onto the surface of a grain eventually react with the CO reservoir despite the activation energy barriers. In this instance, if we let R be the ratio of the accretion rate of D to that of H, the fractionation ratios for the deuterated species are simple powers of R multiplied by a statistical factor, where the power is just the number of D atoms in the isotopomer. The statistical factor expresses the number of possible paths leading to the isotopomer, which, for example, is 3 for CH_2DOH and 1 for CH_3OD. This simple limit is independent of temperature, and so works progressively more poorly as the temperature is raised from 10 K, as can be seen from the temperature dependence in Fig. 1. It also works more poorly for low and intermediate densities, where the CO reservoir does not exist.

5   DISCUSSION

We have shown how a moderately complex system of surface chemical reactions can be solved by the formally exact direct master equation method. This method, or the equivalent Monte Carlo approach, is needed in the so-called accretion limit, which pertains to a situation in which the average abundance of important reactive species on a grain surface is less than unity. In the accretion limit, normal rate equations are likely to be inaccurate, and a more exact method, which treats the discrete nature of the surface populations, is needed. Of the two exact methods used to date, the direct master equation approach offers the possibility of relative ease of implementation in combined gas-grain approaches since it involves the solutions of coupled differential equations.

In order to reach the level of complexity discussed here, we have introduced a new method to limit the number of states considered. This goal is achieved by limiting the *total* number of reactive species considered on a grain. In the current system, which involves 11 reactive species, we have limited consideration to a total number of species in the range 3-4. Of course, this approach only works successfully if the probability for even this number of total species is small, which is what defines the accretion limit.

If one eliminates D and the five deuterium-containing radicals from the 11 reactive species considered here, and replaces them with other reactive species leading to major grain constituents, it is entirely possible that the master equation treatment described here can be extended to study combined gas-grain models of considerable complexity, in which gas-phase abundances change with time. Problems to be solved before this goal becomes a reality include the need to develop a criterion for the smallest number of states
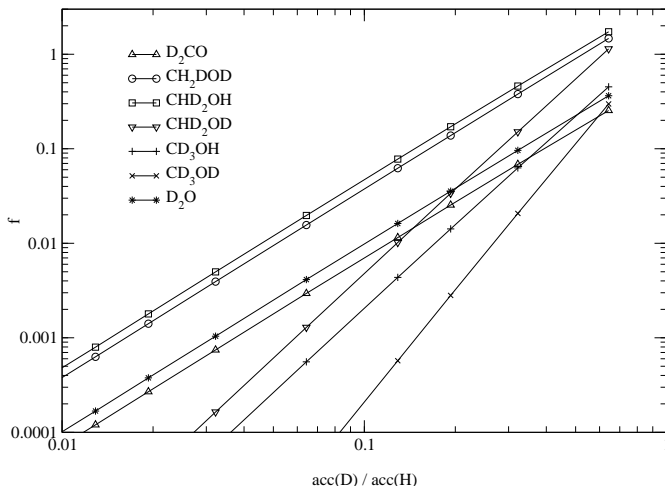
Figure 3. Fractionation ratios f for high density conditions at 10 K vs. acc(D)/acc(H, the ratio of the accretion rate of atomic D to atomic H.

that should be considered, and the related need to determine when and for which species normal rate equations can be utilized. These problems are certain to depend on physical conditions such as grain size and temperature, as well as the rates of diffusion chosen. It would be ideal if a program could be developed to decide these issues as the integration with time proceeds.

Of the deuterated species discussed here, HDCO, D_2CO, CH_3OD, CH_2DOH, CHD_2OH, and HDO have already been detected in interstellar sources. A low-mass protostellar source – IRAS16293-2422 – contains both deuterated isotopomers of formaldehyde, both singly deuterated isotopomers of methanol, and CHD_2OH in the gas phase (Parise et al. 2002). It is likely that at least some of the fractionation occurs on interstellar grains and is followed by evaporation back into the gas (Charnley et al. 1997). As shown by Parise et al. (2002); however, the granular deuteration model presented here and in Caselli et al. (2002), as well as the simpler one in Charnley et al. (1997), does not account quantitatively for all of the observations with any single value of gas-phase D chosen. Clearly, a more complex gas-grain model is needed, in which time-dependent fractionation occurs both in the gas and on dust-particle surfaces. Our current success with the direct master equation method may well allow us to consider such a complex gas-grain system in the future.

REFERENCES

Biham O., Furman I., Pirronello V., Vidali G., 2001, ApJ, 553, 595

Brown P.D., Millar T.J., 2002, MNRAS, 240, 25P

Caselli P., Hasegawa T.I., Herbst E., 1998, ApJ,495, 309

Caselli P., Stantcheva T., Shalabiea O., Shematovich, V.I., Herbst E., 2002, Plan. Sp. Sci., in press

Charnley S.B., 2001, ApJ, 562, L99

Charnley S.B., Tielens A.G.G.M., Rodgers S.D., 1997, ApJ, 482, L203

Green N.J.B., Toniazzo T., Pilling M.J., Ruffle D.P., Bell N., Hartquist, T.W., 2001, A&A, 375, 1111

Hasegawa T.I., Herbst E., Leung C.M., 1992, ApJS, 82, 167

Parise, B. et al., 2002, A&A, in press

Pickles J.B., Williams D.A., 1977, Ap&SS, 52, 443

Roberts H., Herbst E., Millar T.J., 2002, MNRAS, 336, 283

Stantcheva, T., Shematovich V.I., Herbst, E., 2002, A&A, 391, 1069

Tielens A.G.G.M., 1983, A&A, 119, 177

Tielens A.G.G.M., Hagen W., 1982, A&A, 114, 245

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